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(54) Title: UV CURABLE BLEND COMPOSITIONS AND PROCESSES

## (57) Abstract

An ultraviolet curable blend composition comprising (exclusive of any solvent present): (a) about 35 % to about 65 % by weight of a first acrylated aliphatic urethane having a molecular weight of between about 500 and 2000 and formed by the reaction of (i) a first multifunctional acrylate with a molecular weight of between about 190 and 500 and containing at least three polymerizable unsaturated groups per molecule, with (ii) an aliphatic urethane based on a polymer of allyl carbomonocycle diisocyanate with alkanepolyol polyacrylates; (b) about 5 % to about 25 % by weight of a second acrylated aliphatic urethane having a molecular weight of about 1200 to about 2600 and formed by the reaction of a second multifunctional acrylate with a molecular weight of about 110 to about 500 with an aliphatic urethane based on a polyether and having a molecular weight of about 800 to about 2200; (c) about 10 % to about 55 % by weight of a third multifunctional acrylate having a molecular weight of between about 170 and about 1000 and containing at least two polymerizable unsaturated groups per molecule; and (d) a photopolymerization initiator and/or sensitizer. Also described are preferred processes and coated articles involving preferred compositions.

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**UV CURABLE BLEND COMPOSITIONS AND PROCESSES****BACKGROUND OF THE INVENTION**

The present invention relates generally to ultraviolet (UV) cured coatings, and more particularly to UV curable 5 coatings which have demonstrated high gloss, improved scratch and abrasion resistance and other properties excellently suited for overlay and other compositions, as well as to processes of their use and to coated articles resulting therefrom.

10 It is known to the art that conventionally cured coatings have significant disadvantages. In general, the topcoat and the curing agent are applied separately, in a particular sequence and at particular concentration levels. Because both the proportions of the ingredients and the timing of 15 their application is critical, conventionally cured topcoats have been difficult and costly to apply, especially with the efficiency and consistency required in modern commercial applications.

Ultraviolet (UV) cured coatings overcome several 20 disadvantages associated with conventional topcoat finishes. In particular, UV cured topcoats may be premixed so that the polymerization initiator is added to the active ingredients by the manufacturer when the coating is produced, and not by the coating user when the coating is to be applied. Thus, 25 mixing and measurement errors can be avoided and a more consistent product can be obtained.

Despite their many advantages, UV curable coating compositions pose problems which must be addressed. For example, typical UV topcoats are high molecular weight, 30 highly crosslinked films formed from highly reactive acrylate functionality. As such, known UV topcoats have suffered from

-2-

limited durability, have been prone to cured resin shrinkage, and have required high doses of UV light to cure. UV topcoats formulated to overcome these problems typically suffer from a loss of durability or processibility, including 5 diminished scratch resistance, abrasion resistance, weather resistance, chemical resistance, stain resistance, thermal stability and adhesion.

Also, importantly, known UV topcoats upon curing have long proven to form rigid, unflexible and unyieldable 10 coatings. Thus, problems have been experienced in the industry where topcoat overlaid materials have been subjected to conditions causing expansion or contraction of the product during processing or in the field of use. For example, UV topcoats overlaying dark, e.g. black finishes which expand 15 upon heating have been known to crack, form other imperfections, or even cause bending or warping of the substrate due to tensions built up in the materials.

In light of the foregoing, a need exists for a UV curable composition which is conveniently processible and which forms 20 coatings exhibiting improved physical and chemical properties, e.g., improved flexibility, durability, scratch resistance, abrasion resistance, thermal stability, crack resistance, chemical resistance, stain resistance, weather resistance and adhesion.

-3-

SUMMARY OF THE INVENTION

The applicant's invention now addresses these needs and provides in one preferred embodiment a UV curable blend composition comprising: (a) about 35% to about 65% by weight 5 of a first acrylated aliphatic urethane having a molecular weight of about 500 to about 2000 and formed by the reaction of (i) a first multifunctional acrylate with a molecular weight of about 190 to about 500 and containing at least three polymerizable unsaturated groups per molecule, with 10 (ii) an aliphatic urethane based on a polymer of allyl carbomonocycle diisocyanate with alkanepolyol polyacrylates; (b) about 5% to about 25% by weight of a second acrylated aliphatic urethane having a molecular weight of about 1200 to about 2600 and formed by the reaction of a second 15 multifunctional acrylate with a molecular weight of about 110 to about 500 with an aliphatic urethane based on a polyether and having a molecular weight of about 800 to about 2200; (c) about 10% to about 55% by weight of a third multifunctional acrylate having a molecular weight of between about 170 and 20 about 1000 and containing at least two polymerizable unsaturated groups per molecule; and (d) a photopolymerization initiator or sensitizer. The composition can also optionally include a solvent. Unless otherwise specified, percents by weight set forth in this application 25 are calculated exclusive of any solvent present. More preferred compositions can also include suitable light stabilizing agents, e.g., hindered amine and/or benzotriazole derivatives.

Additional preferred embodiments of the invention relate 30 to coated articles and coating processes resulting from and involving the use of applicant's preferred topcoated compositions.

One object of the invention is to provide improved ultraviolet curable compositions demonstrating superior

-4-

chemical and physical properties such as improved flexibility, durability, thermal stability, crack resistance, chemical resistance, stain resistance, weather resistance and adhesion.

5 Another object of the invention is to provide processes for coating or overlaying articles, e.g. coated, e.g. painted, or uncoated plastic or metal parts, so as to improve their physical and chemical properties.

Still another object of the present invention is to  
10 provide a coated or overlaid article exhibiting superior physical and chemical properties, and especially wherein the topcoat is both flexible to resist cracking or other significant deterioration upon expansion of the article or another coating underlaying the topcoat, and durable to avoid  
15 scratching and abrasion of the high gloss surface.

Another object of this invention is to provide coating processes and compositions which enable convenient, consistent and uniform processibility.

Further objects and advantages of the present invention  
20 will be apparent from the following description and claims.

-5-

DESCRIPTION OF THE PREFERRED EMBODIMENT

For the purposes of promoting an understanding of the principles of the invention, reference will now be made to certain embodiments and specific language will be used to describe the same. It will nevertheless be understood that no limitation of the scope of the invention is thereby intended, such alterations, further modifications and applications of the principles of the invention as described herein being contemplated as would normally occur to one skilled in the art to which the invention relates.

As indicated above, one preferred embodiment of this invention relates to a UV curable composition. In this regard, Formula I, set forth below, shows starting materials and compositional ranges for preferred compositions of the invention. The compositional ranges are given as a percent by weight of the composition excluding any solvent which is included.

Formula I:

20	Acrylated aliphatic urethane #1	(35-65%)
	Acrylated aliphatic urethane #2	(5-25%)
	Multifunctional acrylate	(10-55%)
	Photopolymerization initiator	(1-15%)
	Hindered amine light stabilizer	(0.1-7.5%)
25	Hydroxy phenyl benzotriazole	(0.1-7.5%)
	Antioxidant	(0.1%-3%)
	Flow additive	(0.1-5%)

The first acrylated aliphatic urethane according to the present invention contains about 5% to 95% by weight of prereacted multifunctional acrylate and the balance in an aliphatic urethane. More particularly, to obtain the first acrylated aliphatic urethane, a multifunctional acrylate having a molecular weight of about 190 to about 500 and containing at least 3 polymerizable unsaturated groups per molecule (e.g., pentaerythritol triacrylate, diphenyl erythritol tetraacrylate, and trimethylolpropane triacrylate)

-6-

is prereacted with an aliphatic urethane based on a polymer of allyl carbomonocycle diisocyanate with alkanepolyol polyacrylates. The acrylate having at least three polymerizable groups provides an acrylated aliphatic urethane 5 giving final coatings demonstrating good surface hardness, for example as evidenced by steel wool scratch resistance.

The preferred first acrylated aliphatic urethane has a final molecular weight of about 500 to about 2000. More preferably, the first acrylated aliphatic urethane has a 10 molecular weight of about 800 to about 1000, with a molecular weight of about 800 being most preferred in work to date. These preferred acrylated aliphatic urethanes provide coatings of good weather and thermal crack resistance. Further, these acrylated aliphatic urethanes provide 15 advantageous application solids, curing rates and material compatibility.

The first acrylated aliphatic urethane may be obtained commercially. For example, EBECRYL 8301, available from Radcure Specialties, Inc. of Atlanta, Georgia has been highly 20 preferred as the first acrylated aliphatic urethane in work to date.

Exclusive of any solvent present, as indicated above, the first acrylated aliphatic urethane constitutes about 35% to about 65% by weight of the coating composition. More 25 preferably, this acrylated aliphatic urethane makes up about 40% to about 60% of the composition, most preferably about 45-55%. These preferred levels have provided good weather and thermal crack resistance, as well as advantageous scratch and abrasion resistance, viscosity, material capacity and 30 cure rates.

To obtain the second acrylated aliphatic urethane, a multi-functional acrylate having a molecular weight of between about 110 and about 500 (e.g., 1,6 hexanediol diacrylate, hydroxy ethyl acrylate, and trimethylolpropane 35 triacrylate) is prereacted with an aliphatic urethane based

on a polyether and having a molecular weight of about 800 to about 2200 to provide an acrylated aliphatic urethane having a final molecular weight of about 1200 to about 2600.

Acrylated aliphatic urethanes having molecular weights of 5 about 1500 to about 2000 are more preferred, with those having a molecular weight of about 1800 being most preferred to date. These preferred acrylated aliphatic urethanes provide coatings of good weather and thermal crack resistance and as well excellent flexibility. Further, these acrylated 10 aliphatic urethanes provide advantageous application solids, curing rates and material compatibility.

Commercially available acrylated aliphatic urethanes may be used for the second urethane as well. For example, "AB 2010", available from American Biltrite of Lawrenceville, New 15 Jersey, has been a highly preferred as the second acrylated aliphatic urethane in work to date.

Exclusive of any solvent, as indicated above, the acrylated aliphatic urethane constitutes about 5% to about 25% by weight of the composition. More preferably, this 20 acrylated aliphatic urethane makes up about 10% to about 20% of the composition, with a content of about 15-20% being most preferred. These preferred levels have provided good thermal, crack, scratch and abrasion resistance, as well as advantageous viscosity, material capacity and cure rates.

As will be understood, the particular multifunctional acrylate employed in Formula I will depend upon the desired 25 application viscosity and properties. Typical multifunctional acrylates are of the reactive diluent type, have a molecular weight of about 170 to about 1000, and contain at least two polymerizable unsaturated groups per 30 molecule. Representative multifunctional acrylates thus include ethylene glycol di(meth)acrylate, 1,6-hexanediol diacrylate, pentaerythritol triacrylate, pentaerythritol tetra acrylate, trimethylolpropane triacrylate, 35 tetraethleneglycol diacrylate, and the like, and mixtures

-8-

thereof, with light-stable materials, e.g. 1,6-hexanediol diacrylate, being more preferred.

The preferred coating composition includes this multifunctional acrylate in an amount of about 10% to about 5 55% by weight. The range of about 10% to about 40% is more preferred, with about 10%-30% being most preferred in work to date. These preferred levels provide compositions of good compatibility which give coatings of excellent scratch, abrasion, thermal and crack resistance.

10 As those practice in these areas will appreciate, many photopolymerization initiators and/or sensitizers will be suitable for the invention. These include, for instance, benzophenone, benzoin, benzoinmethyl ether, benzoin-n-butyl ether, benzoin-iso-butyl ether, propiophenone, acetophenone, 15 methyphenylgloxylate, 1-hydroxycyclohexyl phenyl ketone, 2,2-diethoxyacetophenone, ethylphenylpyloxylate, phenanthraquinone, and the like, and mixtures thereof. In work thus far, 1-hydroxycyclohexyl phenyl ketone has been more preferred. For additional information on 20 photopolymerization initiators and sensitizers, reference can be made to C. G. Roffey, Photopolymerization of Surface Coatings, Chapter 3: "Photo-initiators and photo-sensitizers", John Wiley & Sons Ltd (1982), which is hereby incorporated by reference.

25 The photopolymerization initiator or sensitizer will be included in an amount sufficient to obtain the desired cure response. In preferred compositions of the invention, the photopolymerization initiator or sensitizer is included in amounts of about 1% to about 15% by weight. The range of 30 about 1% to about 10% is more preferred, with about 5-10% being most preferred so far. As indicated, however, the amount of initiator included will vary based upon many factors such as the cure rate and durability desired.

The composition also preferably includes other materials 35 such as light stabilizers, e.g. suitable hindered amines

and/or benzotriazole derivatives. These materials will be included in varying amounts in accordance with the particular use or application desired. When included, their amounts will be sufficient to provide increased weatherability yet 5 still obtain adequate cure response for the composition. In more preferred compositions, hindered amine, hydroxyphenyl benzotriazole (or other suitable benzotriazole compound) and antioxidants have been included in amounts of about 0.1-7.5%, 0.1-7.5% and 0.1-3.0% respectfully, and in particularly 10 preferred compositions about 1.2%, 0.3% and 0.3% respectively.

As stated, the coating composition also optionally includes a suitable inert solvent. Representative such solvents include ester solvents, e.g. ethyl acetate, butyl acetate, and the like, ketone solvents, e.g. acetone, 15 methylisobutylketone, methylethylketone, and the like, alcohols, e.g. butyl alcohol, and the like, and aromatic solvents, e.g. toluene, xylene, and the like. The amount of solvent included will vary in accordance with the particular application at hand. For instance, for spray applications, 20 higher levels of solvent will typically be included, while for roll applications, lower levels of inert solvent, if any, will be employed. In any event, the inert solvent will constitute from 0% to about 95% by weight of the entire coating composition, and in more preferred coating 25 compositions about 40% to 60%.

As will be understood, the composition can also include other conventional additives. For instance, it can contain polymeric or silicone coating surface improvers, flow improvers, dyes, pigments, antioxidants, flattening agents 30 (e.g. wax-coated or non-wax-coated silica or other inorganic materials), etc. In more preferred compositions, flow improver is included at a level of about 0.3-3%, and in one especially preferred composition, the flow improver Byk 301, available from BYK-CHEMIE, of Wallingford, Connecticut has 35 been included.

-10-

As to its use, the composition can be applied by any conventional coating method as known in the art. For example the composition can be applied directly to the substrate or over another previously-cured (e.g. paints or primers) or uncured (e.g. in the case of tie coats) coating. The material is advantageously used at about 0.3 mils to about 3.0 mils of cured film thickness, with more preferred cured film thicknesses being those around about 1 mil. Preferred thicknesses will provide sufficient film continuity, avoid surface sagging, and promote a satisfactory cure.

Once applied, the coating composition can be cured by irradiation with ultraviolet rays as is known to those skilled in the art. In this regard, the irradiation is continued until curing is complete, with preferred exposure times typically being less than 300 seconds. Curing temperatures can range from room temperature to the heat distortion temperature of the substrate, while curing distances are typically between about 2 and 18 inches from the UV source.

An ultraviolet light source having a wavelength range of between about 1800 Angstroms and 4500 Angstroms is preferred for curing the topcoat. For example, sunlight, mercury lamps, arc lamps, zenon lamps, gallium lamps, and the like may be used, but high pressure or ultrahigh pressure mercury lamps provide particularly advantageous rapid cures.

A high pressure mercury lamp having an intensity of about 30 W/cm to 400 W/cm is preferred, for a total exposure of between about 300 and about 16000 mJ/cm<sup>2</sup> as measured by a compact radiometer at 60 to 1200 mW/cm<sup>2</sup> and about 75 to about 4000 mJ as measured by a UVIMAP, with a preferred exposure of about 3000 mJ/cm<sup>2</sup> as measured by a compact radiometer at 260 mW/cm<sup>2</sup> and about 700 mJ as measured by a UVIMAP. These preferred curing processes have provided good through cure, and have ensured advantageous coatings which resist premature yellowing and demonstrate desirable thermal

-11-

crack resistance. Moreover, these advantageous cures have been achieved over a surprisingly wide range of exposures. Accordingly, the preferred compositions are readily and highly conveniently processible. Previously known UV curable 5 compositions have demonstrated serious deficiencies in this regard, a problem long recognized in the industry leading to increased production costs and wastes of time and materials. Further, the final coatings have the uniquely combined properties of durability, scratch resistance and flexibility, 10 a combination long sought in the coating field.

For the purposes of promoting a further understanding of the invention and its preferred features and advantages, reference will now be made to the following specific examples and tables. It will be understood that these examples and 15 tables are given by way of illustration and are not intended to be restrictive of the invention.

#### EXAMPLE 1

##### Preparation of Preferred UV Curable Coating Composition

In order to prepare a UV curable coating composition in 20 accordance with the invention, items 1 and 2 of Formula II below were charged into a clean stainless steel vessel equipped with a stirrer. Thereafter, ingredients 3 through 9 were added under agitation until a clear homogeneous mixture was obtained. This coating composition was called "Topcoat 25 A."

-12-

Formula II:

		<u>Part by weight</u>
1.	Isopropanol	575.1
2.	Butanol	17.9
5	3. 1-Hydroxycyclohexyl phenyl ketone	26.0
10	4. Hindered amine light stabilizer	5.0
15	5. Benzotriazole	1.0
20	6. Antioxidant	1.0
25	7. Acrylated aliphatic urethane #1*	176.0
30	8. Acrylated aliphatic urethane #2**	78.0
35	9. 1,6 Hexanediol diacrylate	39.0
40	10. Trimethylolpropane triacrylate	78.0
45	11. Flow improver (Byk 301)	3.0

15 \* "EBECRYL 8301", based on polymer of alkyl carbomonocycle diisocyanate with alkanepolyol polyacrylate prereacted with an acrylated polyol.

\*\* "AB 2010," based on a polyether aliphatic urethane prereacted with a multifunctional acrylate.

EXAMPLE 2  
20 Production of Topcoated Plastic Molded Article

The above-described Topcoat A was applied to polycarbonate resin lenses by spray to allow 23 microns of cured coating thickness. Thereafter, the material was irradiated with a high pressure mercury lamp of  $120 \text{ W/cm}^2$ , 25 with the substrate positioned eight inches from the light source for an exposure of  $3000 \text{ mJ/cm}^2$  in air.

The thus obtained topcoated polycarbonate resin lens had a clear appearance. The product was evaluated by exterior decorative standards, and superior results were obtained as 30 set forth in Table 1.

-13-

TABLE I

<u>Evaluated Item</u>	<u>Evaluated Method</u>	<u>Results</u>
Scratch Resistance	0000 Steel Wool Rubs	Passable
Adhesion	Peel Test ASTM	No loss
5 Abrasion Resistance	Taber Abrader, CS-10, 500g load, 300 cycles	Passable
Water Resistance	32 degrees Centigrade, 240 hour immersion	Passable, Secondary adhesion OK
10 Thermal Shock Resist.	4 hrs. water immersion 4 hrs. -29°C Steam blast on scribe	Passable
Heat Resistance	132°C, 2 hrs.	No cracks
15 Resistance to Water & Soap Spotting	Discoloration	Passable
Resist. to Acid Spots	No dulling/color change	Passable
Chemical Resistance	Motor Oil, Tar remover Windshield Wiper Fluid Antifreeze, Motol Fuel	Passable
20 Weather Resistance	EMMA (QUE) 925 MJ, 3.5 years equivalence	Passable
Weather Resistance	Florida exposure 12 months, 45 degrees South	Passable

**EXAMPLE 3**  
Comparative Coating Material #1

The overlay was prepared in the same manner as Topcoat A in Example 1 except the first acrylated aliphatic urethane was replaced with one of a molecular weight of 2279 and labeled "Topcoat B."

**EXAMPLE 4**  
**Comparative Coated Article #1**

Topcoat B was applied and cured as was topcoat A in

-14-

**Example 2.** The resultant product was evaluated by the same conditions as in Example 2, and produced the following results:

TABLE 2

	<u>Evaluated Item</u>	<u>Results of Evaluation</u>
5	Scratch Resistance	Noticeable Scratches
	Adhesion	No loss
	Abrasion Resistance	Unacceptable
	Water Resistance	Passable Secondary adhesion OK
10	Thermal Shock Resistance	Passable
	Heat Resistance	Acceptable
	Resistance to Water & Soap Spotting	Passable
	Resistance to Acid	Passable
15	Spotting	
	Chemical Resistance	Passable
	Weather Resistance	Passable

**EXAMPLE 5**  
**Comparative Coating Material #2**

20        The overlay was prepared in the same manner as Topcoat A in Example 1 except the second acrylated aliphatic urethane was replaced with one of a molecular weight of 1700 (non-polyether type) and labeled "Topcoat C."

**EXAMPLE 6**  
**Comparative Coated Article #2**

Topcoat C was applied and cured as was topcoat A in Example 2. The resultant product was evaluated by the same conditions as in Example 2, and produced the following results:

-15-

TABLE 3

<u>Evaluated Item</u>	<u>Results of Evaluation</u>
Scratch Resistance	Noticeable Scratches
Adhesion	No loss
5 Abrasion Resistance	Unacceptable
Water Resistance	Passable Secondary adhesion OK
Thermal Shock Resistance	Passable
Heat Resistance	Unacceptable
Resistance to Water	Passable
10 & Soap Spotting	
Resistance to Acid	Passable
Spotting	
Chemical Resistance	Passable
Weather Resistance	Passable

15 It was thus demonstrated that the coating compositions of the present invention possess improved physical and chemical properties.

It should be understood that many changes or modifications can be made to adapt the invention to a particular use without changing its basic features. Therefore, while the invention has been described in detail in the foregoing examples and descriptions, the same are to be considered illustrative and not restrictive in character. It is to be understood that preferred embodiments have been described in the preceding examples, and that all changes and modifications that come within the spirit of the invention are desired to be protected.

-16-

CLAIMS

**What is claimed is:**

1. An ultraviolet curable blend composition, comprising, exclusive of any solvent present:
  - 5        about 35% to about 65% by weight of a first acrylated aliphatic urethane, having a molecular weight of between about 500 and 2000 and formed by the reaction of
    - (i) a first multifunctional acrylate with a molecular weight of about 190 to about 500 and containing at least three polymerizable unsaturated groups per molecule, with
      - 10        (ii) an aliphatic urethane based on a polymer of allyl carbomonocycle diisocyanate with alkanepolyol polyacrylates;
    - 15        about 5% to about 25% by weight of a second acrylated aliphatic urethane having a molecular weight of about 1200 to about 2600 and formed by the reaction of
      - (i) a second multifunctional acrylate with a molecular weight of about 110 to about 500, and
        - 20        (ii) an aliphatic urethane based on a polyether and having a molecular weight of about 800 to about 2200; about 10 to about 55% by weight of a third multifunctional acrylate having a molecular weight of about 170 to about 1000 and containing at least two polymerizable unsaturated groups per molecule; and
          - 25        a photopolymerization initiator or sensitizer.
  2. A coating composition according to claim 1 and further comprising a hindered amine light stabilizer.
  3. A coating composition according to claim 2 and further comprising a benzotriazole light stabilizer.
  4. A coating composition according to claim 1 and further comprising an antioxidant.

-17-

5. A coating composition according to claim 1, and also comprising a suitable solvent.

6. A coating composition according to claim 5, which, exclusive of said solvent, is comprised about 40% to about 5 60% by weight of said first acrylated aliphatic urethane

7. A coating composition according to claim 5, which, exclusive of said solvent, is comprised about 10% to about 20% by weight of said second acrylated aliphatic urethane.

8. A coating composition according to claim 5, which, 10 exclusive of said solvent, is comprised about 10% to about 30% of said third multifunctional acrylate.

9. A coating composition according to claim 5, which, exclusive of said solvent, is comprised about 1% to about 15% by weight of said polymerization initiator or sensitizer.

15 10. A coating composition according to claim 9, wherein said first acrylated aliphatic urethane has a molecular weight of about 800 to about 1000.

11. A coating composition according to claim 10, wherein said first acrylated aliphatic urethane is Ebecryl 8301.

20 12. A coating composition according to claim 9, wherein said second acrylated aliphatic urethane has a molecular weight of about 1500 to about 2000.

13. A coating composition according to claim 12, wherein said second acrylated aliphatic urethane is AB 2010.

25 14. A coating composition according to claim 9, and also

-18-

including a hindered amine and a benzotriazole light stabilizer.

15. A coating composition according to claim 14, wherein said benzotriazole light stabilizer is hydroxy phenyl  
5 benzotriazole.

16. A method for forming a coating on an article, comprising the steps of:

(a) applying to the article an ultraviolet curable coating composition including, exclusive of any solvent  
10 present:

about 35% to about 65% by weight of a first acrylated aliphatic urethane having a molecular weight of between about 500 and 2000 and formed by the reaction of  
15 (i) a first multifunctional acrylate with a molecular weight of about 190 to about 500 and containing at least three polymerizable unsaturated groups per molecule, with

20 (ii) an aliphatic urethane based on a polymer of allyl carbomonocycle diisocyanate with alkanepolyol polyacrylates;

about 5% to about 25% by weight of a second acrylated aliphatic urethane having a molecular weight of between about 1200 and 2600 and formed by the reaction of  
25 (i) a second multifunctional acrylate with a molecular weight of about 110 to about 500 and containing at least three polymerizable unsaturated groups per molecule, with

(ii) an aliphatic urethane based on a polyether and having a molecular weight of about 800 to about 30 2200;

about 10% to about 55% by weight of a third multifunctional acrylate having a molecular weight of about 170 to about 1000 and containing at least two

-19-

polymerizable unsaturated groups per molecule; and  
a photopolymerization initiator or sensitizer;

and,

(b) irradiating and thereby curing the applied  
5 composition.

17. A method according to claim 16 wherein said  
ultraviolet curable composition further comprises a solvent,  
and a hindered amine and a benzotriazole light stabilizer.

18. A method according to claim 17 wherein said  
10 benzotriazole light stabilizer is hydroxy phenyl  
benzotriazole.

19. A method according to claim 17 wherein:  
exclusive of said solvent, said curable composition  
is comprised about 40% to about 60% by weight of said first  
15 acrylated aliphatic urethane, about 10% to about 20% by  
weight of said second acrylated aliphatic urethane, and about  
10% to about 30% of said third multifunctional acrylate.

20. A coating composition according to claim 19, wherein  
said first acrylated aliphatic urethane has a molecular  
20 weight of about 800 to about 1000.

21. A coating composition according to claim 20, wherein  
said first acrylated aliphatic urethane is Ebecryl 8301.

22. A method according to claim 19, wherein said second  
acrylated aliphatic urethane has a molecular weight of about  
25 1500 to about 2000.

23. A method according to claim 22, wherein said second  
acrylated aliphatic urethane is AB 2010.

-20-

24. A coated product which comprises a substrate and a top coating layer, characterized in that said top coating layer is a cured layer of an ultraviolet curable topcoat composition comprising, exclusive of any solvent present:

5 about 35% to about 65% by weight of a first acrylated aliphatic urethane, having a molecular weight of between about 500 and 2000 and formed by the reaction of

(i) a first multifunctional acrylate with a molecular weight of about 190 to about 500 and containing 10 at least three polymerizable unsaturated groups per molecule, with

(ii) an aliphatic urethane based on a polymer of allyl carbomonocycle diisocyanate with alkanepolyol polyacrylates;

15 about 5% to about 25% by weight of a second acrylated aliphatic urethane having a molecular weight of about 1200 to about 2600 and formed by the reaction of

(i) a second multifunctional acrylate with a molecular weight of about 110 to about 500, and

20 (ii) an aliphatic urethane based on a polyether and having a molecular weight of about 800 to about 2200; about 10% to about 55% by weight of a third

multifunctional acrylate having a molecular weight of about 170 to about 1000 and containing at least two polymerizable 25 unsaturated groups per molecule; and

a photopolymerization initiator or sensitizer.

25. A coated product according to claim 24, wherein said ultraviolet curable topcoat composition further comprises a solvent, and a hindered amine and a benzotriazole light 30 stabilizer.

26. A coated product according to claim 25, and also comprising an underlay coating between said top coating layer and said substrate.

-21-

27. A coated product according to claim 26 wherein:  
exclusive of said solvent, said ultraviolet curable  
topcoat composition is comprised about 40% to about 60% by  
weight of said first acrylated aliphatic urethane, about 10%  
5 to about 20% by weight of said second acrylated aliphatic  
urethane and about 10% to about 30% by weight of said third  
multifunctional acrylate.

28. A coated product according to claim 27, wherein said  
first acrylated aliphatic urethane has a molecular weight of  
10 about 800 to about 1000.

29. A coated product according to claim 28, wherein said  
first acrylated aliphatic urethane is Ebecryl 8301.

30. A coated product according to claim 27, wherein said  
second acrylated aliphatic urethane has a molecular weight of  
15 about 1500 to about 2000.

31. A coated product according to claim 29, wherein said  
second acrylated aliphatic urethane is AB 2010.

## INTERNATIONAL SEARCH REPORT

I. National application No.

PCT/US92/02710

## A. CLASSIFICATION OF SUBJECT MATTER

IPC(5) :Please See Extra Sheet.

US CL :522/075,096,174; 427/054.1; 428/423.1; 524/379,391; 528/066

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : NONE

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

APS: EBECRYL 8301, ALLYL (METH)ACRYLOYL; ALLYL DIISOCYANATE AND (METH) ACRYLATE; URETHANE OR POLYURETHANE

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US, A, 4,287,323 (TEFERTILLER ET AL.) 01 September 1981, See columns 1-5, column 6, lines 22-54 and column 7, lines 6-10.	1,4-10,12 16,24
Y	US, A, 4,717,739 (CHEVREUX ET AL.) 05 January 1988, See column 4, column 5, lines 12-17 and column 7, lines 5-15.	1,4-10,12, 16,24
Y	US, A, 4,065,587 (TING) 27 December 1977, See columns 2-4.	1,4-10,12, 16,24
Y	US, A, 4,393,187 (BOBA ET AL.) 12 July 1983, See columns 2-7 and the Example.	1,4-10,12, 16,24
Y	US, A, 4,128,600 (SKINNER ET AL.) 05 December 1978, See column 7, lines 43-59.	1,6,10,16, 24
Y	US, A, 4,511,596 (BERNER) 16 April 1985, See Abstract, column 20, lines 59-68 and column 23, lines 61-68.	2-4,14,15, 17,18,25- 28 & 30
A	US, A, 4,608,409 (COADY ET AL.) 26 August 1986, See the Abstract.	1,4-10,12, 16,24

 Further documents are listed in the continuation of Box C. See patent family annex.

* Special categories of cited documents:	"T"	later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"A" document defining the general state of the art which is not considered to be part of particular relevance	"X"	document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"E" earlier document published on or after the international filing date	"Y"	document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	"&"	document member of the same patent family
"O" document referring to an oral disclosure, use, exhibition or other means		
"P" document published prior to the international filing date but later than the priority date claimed		

Date of the actual completion of the international search

06 JULY 1992

Date of mailing of the international search report

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## INTERNATIONAL SEARCH REPORT

International application No.  
PCT/US92/02710

## C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US, A, 4,463,169 (IRVING) 31 July 1984. See the Abstract.	1,4-10,12,16,24

Form PCT/ISA/210 (continuation of second sheet)(July 1992)\*

# INTERNATIONAL SEARCH REPORT

In. national application No.  
PCT/US92/02710

## A. CLASSIFICATION OF SUBJECT MATTER: IPC (5):

B32B 27/36; B05D 3/06; C08L 75/08,75/14,75/16; C08K 5/05; C08F 2/50, 220/36,265/06,283/04; C08G 69/44.